



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 253 566 B1**

EUROPEAN PATENT SPECIFICATION

Date of publication of patent specification: **24.03.93** Int. Cl.⁵: **C11D 17/04**

Application number: **87306045.3**

Date of filing: **08.07.87**

Laundry products.

Priority: **12.07.86 GB 8617058**

Date of publication of application:
20.01.88 Bulletin 88/03

Publication of the grant of the patent:
24.03.93 Bulletin 93/12

Designated Contracting States:
BE DE FR GB IT NL

References cited:
EP-A- 0 079 248
EP-A- 0 118 313
US-A- 4 082 678

Proprietor: **THE PROCTER & GAMBLE COMPANY**

**One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)**

Designated Contracting States:
BE DE FR GB IT NL

Proprietor: **Procter & Gamble Limited**
Hedley House
Gosforth Newcastle upon Tyne NE99
1EE(GB)

Designated Contracting States:
GB

Inventor: **Talkes, Brian Edward**
Manor House
Mitford Northumberland(GB)
Inventor: **Lowery, Colin James**
8 Marquis Avenue St John's Estate
Westerhope Newcastle upon Tyne(GB)
Inventor: **Tunnah, Brian George**
134 Ringwood Drive Parkside Glade
Cramlington Northumberland(GB)

Representative: **Brooks, Maxim Courtney et al**
Procter & Gamble (NTC) Limited Whitley
Road Longbenton
Newcastle-upon-Tyne NE12 9TS (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 253 566 B1

Description

The invention relates to laundry products. In particular, it relates to laundry products suitable for cleaning or conditioning fabrics and which contain a laundry composition in particulate form.

There have been a number of proposals in the art for marketing granular detergent and other laundry compositions in packages, each of which contain a suitable amount of the composition for a single wash under conventional conditions. These proposals include using closed bags of water-soluble film-forming materials such as polyvinylalcohol and methyl cellulose; and also water-insoluble but water-permeable materials such as paper and woven or non-woven fabrics. The latter approach in particular has a number of attractions; for example, it ensures that the detergent ingredients are only released into the wash liquor in solubilized or dispersed form; it avoids loss of detergent within the dispenser and sump of the washing machine; and it provides for greater convenience in use. Despite the technical and consumer advantages, however, packages of this type have not been commercially successful.

A major problem of the usual film-forming materials such as polyvinyl alcohol is their tendency to gel when placed in solutions containing laundry detergent compositions. This leads not only to a reduced rate of film solubilization but also to messy, gel-like residues which deleteriously affect solubility of the active composition and which also have a tendency to deposit on the laundry. Proposals for enhancing the solubility of polyvinyl alcohol films have been made (EP-A-0079712) but such proposals relate to chemical modification of the polymer and are relatively complex. At the same time EP-A-0079712 discounted the use of poly(ethylene oxide) as the film-forming material for detergent products on the basis that films of this material tend to absorb moisture too readily and become tacky. Fabric conditioning articles comprising low molecular weight polymeric films, including poly(ethylene oxide), are disclosed in US-A-4082678.

The moisture-sensitivity of poly(ethylene oxide) films is of course well-known in the packaging arts and a moisture-barrier film such as polyethylene is commonly recommended to protect the poly(ethylene oxide) from accidental contact with water and from excessive humidity. Polyethylene moisture barrier films are clearly unacceptable in a laundry product context, however, both from the viewpoint of dissolution of the active composition and from the residue viewpoint.

Accordingly, the present invention provides a laundry product containing pre-measured amounts of laundry actives in a convenient pouch-form having acceptable storage characteristics and freedom from tackiness under high humidity conditions as well as excellent product dissolution characteristics under typical European and US laundering conditions.

According to the present invention, there is provided a laundry product which comprises a particulate laundry composition releasably contained within a single- or multi-compartment sachet formed of or comprising a thermoplastic film of water-soluble poly(ethylene oxide) having a viscosity-average molecular weight of at least 1,000,000 said film having an outer covering of a flexible, water-insoluble but water-permeable non-woven, textile or paper sheet-like material.

The laundry products of the invention comprise a sachet and a particulate laundry composition. In preferred embodiments the laundry composition takes the form of a particulate detergent composition and the laundry product is designed for addition to the wash cycle of a domestic automatic washing machine.

The sachet itself is formed of or comprises a thermoplastic film of poly(ethylene oxide) having a molecular weight of at least 1,000,000, and especially at least 3,000,000, molecular weight being defined herein as the average molecular weight of the resin used for making the poly(oxyethylene) films and derived from rheological measurements (see the book Poly(ethylene oxide) by F E Bailey and J V Koleske, Academic Press, 1976, pages 46 to 49 and Union Carbide Corporation Technical Bulletin F-42933, Polyox-(R) Water-Soluble Resins). The thickness of the film is preferably from 0.001 to 0.003 in (0.025 to 0.075mm). The film preferably also has a tensile strength (MD) of at least 2000 psi (13,788kPa), a tensile strength (TD) of at least 1500 psi (10,341kPa), an elongation (MD) of 200-100% and an elongation (TD) of 300-700%. In the above, MD and TD refer to machine direction and transverse direction respectively.

In the laundry products of the invention, the poly(ethylene oxide) film has an outer covering of a flexible sheet-like material. The sheet-like material may be made of paper, woven or non-woven fabrics or the like and should be water-insoluble but water-permeable. In highly preferred embodiments, the sheet-like material is apertured in order to effect rapid release of the laundry actives in dissolved or dispersed form. Preferably, the aperture density is from 3 to 30, more preferably from 13 to 26, especially from 16 to 23 apertures per sq cm of sheet and the apertures preferably have, on average, a width of from 0.5mm to 5mm and a length of from 0.8mm to 5mm. The apertures themselves are generally symmetrical about a longitudinal axis (ie they have mirror symmetry) and preferably have, on average, a width of from 0.7 to 2.5mm and a length of from 1.7mm to 4mm. The area of the apertures, on the other hand, is preferably from 0.7mm² to 25mm², more preferably from 0.8mm² to 10mm², and the ratio of length:width is from 1:1

up to preferably 6:1, more preferably 4:1.

The apertures can be elongate in shape (for example, generally elliptical or diamond-shaped) in which case they preferably have a width of from 0.8mm to 1.5mm and a length of from 2mm to 3.5mm. Alternatively, the apertures can be generally circular with a diameter of up to 5mm, preferably 1 to 4mm. In preferred embodiments, however, the apertures are generally square-shaped with a side dimension of from 1 to 2.5mm. As used herein, "length" refers to the dimension of the principal (ie longest) longitudinal axis; and "width" is the maximum dimension perpendicular to this axis.

The basis weight of the water-insoluble cover sheet is preferably from 10 to 70 grams/sq metre, more preferably from 20 to 50 grams/sq metre. Preferred materials for use herein are apertured nonwoven fabrics which can generally be defined as adhesively or thermo-bonded fibrous or filamentous products, having a web or carded fibre structure (where the fibre strength is suitable to allow carding) or comprising fibrous mats, in which the fibres of filaments are distributed haphazardly or in random array (i.e. an array of fibres in a carded web wherein partial orientation of the fibres is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibres or filaments can be natural (e.g. wool, silk, wood pulp, jute, hemp, cotton, linen, sisal, or ramie), synthetic (e.g. rayon, cellulose, ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters) or mixtures of any of the above.

Generally, non-woven cloths can be made by air or water laying processes in which the fibres or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fibre-laden air or water is passed. The deposited fibres or filaments are then adhesively or thermo-bonded together, dried cured and otherwise treated as desired to form the non-woven cloth. Alternatively, the non-woven cloths can be spin-bonded, spin-laced or melt-blown.

Preferably, the non-woven cloth is made from cellulosic fibres, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant such as sodium oleate. The non-woven cloth preferably also has a content of a polyolefin such as polypropylene to allow for heat sealing to the poly(ethylene oxide) film. Preferably the fibres are from 4 to 50mm, especially from 8mm to 20mm, in length and are from 0.111 to 0.556 tex (1 to 5 denier). Preferably the fibres are at least partially orientated haphazardly, particularly substantially haphazardly, and are adhesively bonded together with hydrophobic or substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. In highly preferred embodiments, the cloth comprises from 75% to 88%, especially from 78% to 84% fibre and from 12% to 25%, especially from 16% to 22% hydrophobic binder-resin polymer by weight and has a basis weight of from 10 to 70, preferably from 20 to 50g/m². Suitable hydrophobic binder-resins are ethylacrylate resins such as Primal(RTM) HA24, Rhoplex(RTM) HA8 and HA16 (Rohm and Haas, Inc) and mixtures thereof.

The substrate apertures, which extend between opposite surfaces of the substrate, are normally in a pattern and are formed during lay-down of the fibres to produce the substrate. Exemplary apertured non-woven substrates are disclosed in US-A-3,741,724, US-A-3,930,086 and US-A-3,750,237.

An example of an apertured non-woven substrate suitable herein is a polypropylene-containing regenerated cellulose sheet of 0.166 tex (1.5 denier) fibres bonded with Rhoplex(RTM) HA 8 binder (fibre:binder ratio of about 77:23) having a basis weight of about 35 g/m² and about 17 apertures/cm². The apertures are generally elliptical in shape and are in side-by-side arrangement. The apertures have a width of about 0.9mm and a length of about 2.5mm measured in a relaxed condition. Another highly preferred substrate based on 0.166 tex (1.5 denier) regenerated cellulose fibres with Rhoplex(RTM) HA8 binder has a fibre:binder ratio of about 82:18, a basis weight of about 35g/m², and about 22 apertures/cm². In this example, the apertures are generally square-shaped with a width of about 1.1mm. The apertures are again disposed in side-by-side arrangement.

If desired, the sachet can be provided with more than one separate compartment for different laundry ingredients, or the sachets may be formed in a conjoined manner, for example in a strip with individual sachets separated by perforations to facilitate dosing of different numbers of the sachets as appropriate for the wash conditions. The use of multi-compartment sachets facilitates the use of laundry ingredients in laundry compositions, whilst avoiding encapsulation or other treatment to prevent contact between such ingredients in a single composition.

In one preferred embodiment of the invention, the or each compartment of the sachet comprises a closed inner pouch formed of the poly(ethylene oxide) film and containing a quantity of the particulate laundry composition, the closed inner pouch being contained within and covered by an outer pouch formed of the water-insoluble but water-permeable sheet-like material. In another embodiment, the sachet takes the form of a laminate comprising two inner layers of the poly(ethylene oxide) film and two outer layers of the non-woven, textile or paper material, the inner and outer layers of the laminate being bonded together along

seal lines arranged so as to define one or more closed, non-connecting pockets between the two inner layers of the laminate. The precise disposition of the seal lines, of course, will depend upon the desired design of sachet. In general, however, the laminate will be sealed along all its free edges and it may also have additional transverse or longitudinal seals as appropriate. A suitable method of bonding is heat-sealing.

5 It will be understood that laminated structures in which each inner layer of the laminate is bonded continuously to its corresponding outer layer are also within the scope of the invention.

Moreover, it will also be understood that the sachet can be formed from a laminated substrate comprising a single ply of the poly(ethylene oxide) film and a single ply of the non-woven, textile or paper material, the laminated substrate being folded during manufacture of the laundry product so as to provide in
10 the final product two inner layers of poly(ethylene oxide) film and two outer layers of the non-woven, textile or paper material. Such a design facilitates recovery of the water-insoluble sheet by the housewife after use.

The laundry products of the invention also comprise a particulate laundry composition, especially a granular or powder-form detergent composition incorporating organic surfactant, detergency builder and detergency adjuncts such as bleaches etc.

15 A wide range of organic surfactants can be incorporated in the laundry composition inclusive of anionic, cationic, ampholytic and zwitterionic deterative surfactants and mixtures thereof. The total level of these materials is generally from about 2% to about 40%, preferably from about 5% to about 25% by weight of the total laundry composition.

Suitable synthetic anionic surfactants are water-soluble salts of C_8 - C_{22} alkyl benzene sulphonates, C_8 -
20 C_{22} alkyl sulphates, C_{10} - C_{18} alkyl polyethoxy ether sulphates, C_8 - C_{24} paraffin sulphonates, alpha- C_{12} - C_{24} olefin sulphonates, alpha-sulphonated C_6 - C_{20} fatty acids and their esters, C_{10} - C_{18} alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, especially those prepared from coconut oil, C_8 - C_{12} alkyl phenol polyethoxy ether sulphates, 2-acyloxy C_9 - C_{23} alkane-1-sulphonate, and beta-alkyloxy C_8 - C_{20} alkane sulphonates.

25 A particularly suitable class of anionic surfactants includes water-soluble salts, particularly, the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups).

30 Examples of this group of synthetic detergents are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_8 - C_{18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from about 9 to about 15, especially about 11 to about 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.-A-2,220,099 and U.S.-A-2,477,383
35 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS, and C_{12} - C_{15} methyl branched alkyl sulphates.

40 The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred.

Suitable fatty acid soaps herein can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkyloammonium salts of higher fatty acids containing from about 8 to about 24, preferably
45 from about 10 to about 22 and especially from about 16 to about 22 carbon atoms in the alkyl chain. Fatty acids in partially neutralized form are also suitable for use herein, especially in liquid compositions. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

50 Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from about 5:1 to about 1:5, preferably from about 5:1 to about 1:1, more preferably from about 5:1 to about 1.5:1. Especially preferred is a mixture of an alkyl benzene sulphonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium; and either an alkyl sulphate having from 10 to 20, preferably 12 to 18
55 carbon atoms in the alkyl radical or an ethoxy sulphate having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, having an alkali metal cation, preferably sodium.

Nonionic surfactants suitable herein are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from about 8 to 17, preferably from about 9.5 to 13.5, more preferably from about 10 to about 12.5.

Examples of suitable nonionic surfactants include the condensation products of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to about 40 moles, preferably 2 to about 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols(RTM), Dobanols(RTM) and Neodols(RTM) which have about 25% 2-methyl branching (Lutensol(RTM) being a Trade Name of BASF, Dobanol(RTM) and Neodol(RTM) being Trade Names of Shell), or Synperonics(RTM), which are understood to have about 50% 2-methyl branching (Synperonic(RTM) is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol(RTM) 45-4, Dobanol(RTM) 45-7, Dobanol(RTM) 45-9, Dobanol(RTM) 91-2.5, Dobanol(RTM) 91-3, Dobanol(RTM) 91-4, Dobanol(RTM) 91-6, Dobanol(RTM) 91-8, Dobanol(RTM) 23-6.5, Synperonic(RTM) 6, Synperonic(RTM) 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

Other suitable nonionic surfactants include the condensation products of C_6 - C_{12} alkyl phenols with from about 3 to 30, preferably 5 to 14 moles of ethylene oxide, and the compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol, such synthetic nonionic detergents being available on the market under the Trade Name of "Pluronic(RTM)" supplied by Wyandotte Chemicals Corporation.

Especially preferred nonionic surfactants for use herein are the C_9 - C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{12} - C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants and surfactants of a semi-polar nature, for example amine oxides. Suitable quaternary ammonium surfactants are selected from mono C_8 - C_{16} , preferably C_{10} - C_{14} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl and the corresponding di- C_6 - C_{10} N-alkyl or alkenyl ammonium surfactants. Suitable amine oxides are selected from mono C_8 - C_{20} , preferably C_{10} - C_{14} N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are again substituted by methyl, hydroxyethyl or hydroxypropyl.

Suitable builder salts useful herein can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. The level of these materials is generally from about 15% to about 90%, preferably from about 20% to about 60% by weight of the total laundry composition. Non-limiting examples of suitable water-soluble, inorganic alkaline builder salts include the alkali metal carbonates, borates, phosphates, pyrophosphates, triphosphates and bicarbonates.

Organic builder/chelating agents that can be incorporated include organic polycarboxylates and aminopolycarboxylates and their salts, organic phosphonate derivatives such as those disclosed in US-A-3,213,030, US-A-3,433,021, US-A-3,292,121 and US-A-2,599,807, and carboxylic acid builder salts such as those disclosed in US-A-3,308,067.

Preferred chelating agents include citric acid, nitrilotriacetic (NTA) and ethylenediamine tetra acetic acids (EDTA), hydroxyethylethylenediaminetriacetic acid (HEEDTA), nitrilo(trimethylene phosphonic acid) (NTMP), ethylenediamine tetra(methylene phosphonic acid) (EDTMP) and diethylenetriamine penta-(methylene phosphonic acid) (DETPMP) and salts thereof. Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in CA-A-755,038, e.g. a ternary mixture of sodium triphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

A further class of builder salts is the insoluble aluminosilicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation $Na_z(AlO_2)_x(SiO_2)_y \cdot xH_2O$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5 and x is an integer from about 15 to about 264. Compositions

incorporating builder salts of this type form the subject of GB-A-1,429,143, DE-A-2,433,485, and DE-A-2,525,778.

The laundry compositions herein can be supplemented by all manner of detergent and laundering components.

- 5 An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate is preferably from about 3% to about 15% by weight of the total composition. Suitable silicate solids have a molar ratio of $\text{SiO}_2/\text{alkali metal}_2\text{O}$ in the range from about 0.5 to about 3.3, more preferably from about 1.0 to about 2.0.

- The laundry compositions herein can also contain bleaching components. In general, the bleach is selected from inorganic peroxy salts, hydrogen peroxide, hydrogen peroxide adducts, and organic peroxy acids and salts thereof. Suitable inorganic peroxygen bleaches include sodium perborate mono- and tetrahydrate, sodium percarbonate, sodium persulfate, urea-hydrogen peroxide addition products and the clathrate $4\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot 1\text{NaCl}$. Suitable organic bleaches include peroxydicarboxylic acid, peroxyoctanoic acid, peroxydecanoic acid, diperoxydodecanedioic acid, diperoxyazelaic acid, mono- and diperoxyphthalic acid and mono- and diperoxyisophthalic acid and salts (especially the magnesium salts) thereof. The bleaching agent is generally present at a level of from about 5% to about 35%, preferably from about 10% to about 25% by weight of total laundry composition. Peroxyacid bleach precursors suitable herein are disclosed in UK-A-2040983, highly preferred being peracetic acid bleach precursors such as tetraacetylene diamine, tetraacetylmethylenediamine, tetraacetylhexylenediamine, sodium p-acetoxylbenzene sulphonate, tetraacetylglucosyl, pentaacetylglucose, octaacetylactose, methyl O-acetoxylbenzoate, sodium 3,5,5-trimethylhexanoyloxybenzene sulfonate, sodium 3,5,5-trimethylhexanoyloxybenzoate, sodium 2-ethylhexanoyloxybenzenesulfonate, sodium nonanoyloxybenzenesulfonate and sodium octanoyloxybenzenesulfonate. The level of bleach precursor is generally from about 0.5% to about 10%, preferably from about 1% to about 6% by weight of the total composition.

- 25 Other optional components of the compositions herein include suds suppressors, enzymes, fluorescers, photoactivators, soil suspending agents, anti-caking agents, pigments, perfumes, fabric conditioning agents etc.

- Suds suppressors are represented by materials of the silicone, wax, vegetable and hydrocarbon oil and phosphate ester varieties. Suitable silicone suds controlling agents include polydimethylsiloxanes having a molecular weight in the range from about 200 to about 200,000 and a kinematic viscosity in the range from about 20 to about 2,000,000 mm^2/s , preferably from about 3000 to about 30,000 mm^2/s , and mixtures of siloxanes and hydrophobic silanated (preferably trimethylsilanated) silica having a particle size in the range from about 10 nm to about 20 nm and a specific surface area above about 50 m^2/g . Suitable waxes include microcrystalline waxes having a melting point in the range from about 65°C to about 100°C, a molecular weight in the range from about 4000-10000, and a penetration value of at least 6, measured at 77°C by ASTM-D1321, and also paraffin waxes, synthetic waxes and natural waxes. Suitable phosphate esters include mono- and/or di- C_{16} - C_{22} alkyl or alkenyl phosphate esters, and the corresponding mono- and/or di alkyl or alkenyl ether phosphates containing up to 6 ethoxy groups per molecule.

- Enzymes suitable for use herein include those discussed in US-A-3,519,570 and US-A-3,533,139. Suitable fluorescers include Blankophor(RTM) MBBH (Bayer AG) and Tinopal(RTM) CBS and EMS (Ciba Geigy). Photoactivators are discussed in EP-A-57088, highly preferred materials being zinc phthalocyanine, tri- and tetra-sulfonates. Suitable fabric conditioning agents include smectite-type clays as disclosed in GB-A-1400898 and di- C_{12} - C_{24} alkyl or alkenyl amines and ammonium salts.

- Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Preferred polymers include copolymers or salts thereof of maleic anhydride with ethylene, methylvinyl ether, acrylic acid or methacrylic acid, the maleic anhydride constituting at least about 10 mole percent, preferably at least about 20 mole percent of the copolymer. These polymers are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

- In the preferred embodiments, the laundry compositions herein have a bulk density of at least about 0.5g/cc, preferably at least about 0.6g/cc, and more preferably at least about 0.7g/cc. In the case of multi-compartment sachets, bulk density is measured on an individual compartment basis. Thus, the contents of at least one compartment or set of compartments should meet the preferred bulk density limitations. In highly preferred embodiments, however, at least about 50%, and more preferably at least about 80% by weight of the laundry composition is in one or more compartments meeting the bulk density parameters.

The laundry compositions are preferably made by spray-drying an aqueous slurry comprising anionic surfactant and detergency builder to a density of at least about 0.3g/cc, spraying-on nonionic surfactant, where present, and comminuting the spray-dried granules in for example a Patterson-Kelley twin shell blender. The aqueous slurry for spray drying preferably comprises from about 30% to about 60% water and from about 40% to about 70% of the detergency builder; it is heated to a temperature of from about 60°C to about 90°C and spray dried in a current of air having an inlet temperature of from about 200°C to about 400°C, preferably from about 275°C to about 350°C, and an outlet temperature of from about 95°C to about 125°C, preferably from about 100°C to about 115°C. The weight average particle size of the spray dried granules is from about 0.15 to about 3mm, preferably from about 0.5mm to about 1.4mm. After comminution, the weight average particle size is from about 0.1 to about 0.5mm, preferably from about 0.15 to about 0.4mm.

In the final laundry product, the total volume of laundry composition will normally lie in the range of from 60 to about 400cc, preferably from about 100 to 300cc and more preferably from about 200 to about 260cc, product volume being defined as product weight/bulk density. The volume of composition in any given compartment of the sachet will naturally depend on the product design and in particular on the number of compartments per sachet. In twin compartment sachets, for example, each compartment will preferably comprise from about 50 to about 150cc, more preferably from about 100 to about 130cc of product. Multi-compartment sachets containing as many as 25 to 100 compartments are within the scope of the invention, however, in which case the compartments can contain individually from about 1cc to about 15cc, preferably from about 3cc to about 9cc of product.

In the Examples, the abbreviations used have the following designation:

LAS	: Linear C ₁₂ alkyl benzene sulphonate
TAS	: Tallow alkyl sulphate
C _{14/15} AS	: Sodium C ₁₄ -C ₁₅ alkyl sulphate
TAE _n	: Hardened tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
C ₁₂ TMAB	: C ₁₂ alkyl trimethyl ammonium bromide
Dobanol(RTM) 45-E-7	: A C ₁₄ -C ₁₅ primary alcohol condensed with 7 moles of ethylene oxide, marketed by Shell
Clay	: Sodium montmorillonite
INOBS	: Sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate
TAED	: Tetraacetylenediamine
DPDA	: Diperoxydodecanedioic acid (30%); boric acid/ sulphate mixture (70%)
PPA	: Peroxyphthalic acid, magnesium salt
Silicone/Silica	: 85:15 mixture of polydimethylsiloxane and silanated silica prilled with STPP and TAE ₈₀
Enzyme	: Savinase(RTM) prills
STPP	: Sodium tripolyphosphate
Zeolite	: Zeolite 4A
Metasilicate	: Sodium metasilicate
Na ₂ CO ₃	: Sodium carbonate
Silicate	: Sodium silicate (SiO ₂ :Na ₂ O = 1.6:1)
Perborate	: Anhydrous sodium perborate bleach of empirical formula NaBO ₂ .H ₂ O ₂
Percarbonate	: Sodium percarbonate
MA/AA	: Maleic acid/acrylic acid copolymer, 1:3 mole ratio, m.wt. 70,000
EDTA	: Sodiummethylenediaminetetraacetate
Brightener	: Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2,2'-disulphonate
EDTMP	: Ethylenediamine tetra(methylene phosphonic acid), marketed by Monsanto, under the Trade name Dequest 2041

EXAMPLES I TO VI

Six laundry products are prepared as follows:

- 55 A base powder composition is first prepared by mixing all components except Dobanol(RTM) 45E7, bleach, bleach activator, enzyme, suds suppressor, phosphate and carbonate in a crutcher as an aqueous slurry at a temperature of about 55°C and containing about 35% water. The slurry is then spray dried at a gas inlet temperature of about 330°C to form base powder granules and the granules are comminuted in a

Patterson-Kelley twin shell blender. The bleach activator where present, is then admixed with TAE₂₅ as binder and extruded in the form of elongate particles through a radial extruder as described in EP-A-62523. The bleach activator noodles, bleach, enzyme, suds suppressor, phosphate and carbonate are then dry-mixed with the base powder composition and finally Dobanol 45E7 is sprayed into the final mixture. Each composition had a bulk density of about 0.7g/cc.

	I	II	III	IV	V	VI
LAS	5	8	8	3	4	9
TAS	-	-	3	-	4	3
C _{14/15} AS	5	8	-	1	-	-
TAE ₂₅	0.5	0.3	0.5	0.2	0.8	0.5
C ₁₂ TMAB	2	-	-	-	2	-
Dobanol(RTM) 45-E-7	2	2	4	10	4	-
Clay	-	6	-	-	4	7
INOBS	-	2	4	-	-	3
TAED	3	-	0.5	-	2	-
Silicone/Silica	0.2	0.2	0.4	0.8	0.4	0.5
Enzyme	0.5	0.6	0.7	0.8	0.5	0.6
STPP	9	-	25	-	24	10
Zeolite	12	18	-	22	-	10
Metasilicate	-	-	-	-	-	5
Na ₂ CO ₃	5	-	8	-	-	5
Silicate	5	6	10	6	6	-
Perborate	10	-	14	-	-	12
Percarbonate	-	-	-	-	20	-
MA/AA	4	3	2	2	4	2
EDTA	0.5	0.5	0.5	0.5	0.5	0.5
Brightener	0.2	0.2	0.2	0.2	0.2	0.2
EDTMP	0.2	0.1	0.2	0.3	0.2	0.1
Sulphate, moisture	To 100					

A twin-compartment sachet is made from a poly(ethylene oxide) film having an average molecular weight of about 4,000,000, a tensile strength of about 3000 psi (20,682kPa) and an elongation of about 450%, and a non-woven fabric formed of 100% unbleached crimped rayon fibres of 0.166 tex (1.5 denier) bonded with 18% polyacrylate builder, the non-woven fabric having a basis weight of 35g/m² and containing 22 1.1mm x 1.1mm square-shaped apertures/cm². The sachet is made by superposing a sheet of the poly(ethylene oxide) film and a sheet of the non-woven fabric, each sheet measuring 120mm x 80mm, folding the superposed sheets midway along the long dimension with the poly(ethylene oxide) film inwards, heat-sealing the superposed sheets along the two opposing free edges and along a longitudinal seam parallel to and half-way between the two opposing edges, filling the two compartments with 120cc each of detergent composition I and then sealing along the open edge of the sachet. The procedure is then replicated five times using composition II to VI respectively. The resulting laundry products have acceptable storage characteristics and freedom from tackiness under high humidity conditions as well as excellent dissolution characteristics under typical European and US laundering conditions.

Examples VII to VIII

The procedure of Examples I to VI is repeated using compositions II and IV but in each instance, only one compartment of the twin-compartment sachet is filled with the detergent composition, the other compartment being filled with 14g of 30% active DPDA (Example VII) or 10g of PPA (Example VIII) respectively. The resulting products again have acceptable storage characteristics and freedom from tackiness under high humidity conditions as well as excellent dissolution characteristics under typical European and US laundering conditions.

Claims

1. A laundry product which comprises a particulate laundry composition releasably contained within a single- or multi-compartment sachet formed of or comprising a thermoplastic film of water-soluble poly-(ethylene oxide) having a viscosity-average molecular weight of at least 1,000,000, said film having an outer covering of a flexible, apertured, water-insoluble but water-permeable non-woven, textile or paper sheet-like material.
2. A product according to Claim 1 wherein the poly(ethylene oxide) has a viscosity-average molecular weight of at least 3,000,000.
3. A product according to Claim 1 or 2 wherein the apertured sheet-like material has an aperture density of from 3 to 30 apertures per sq cm and wherein the apertures, on average, have an area of from 0.7mm² to 25mm².
4. A product according to any of Claims 1 to 3 wherein the or each compartment comprises a closed inner pouch formed of the poly(ethylene oxide) film and containing a quantity of the particulate detergent composition, the closed inner pouch being contained within and covered by an outer pouch formed of the water-insoluble but water-permeable sheet-like material.
5. A product according to any of Claims 1 to 3 wherein the sachet is in the form of a laminate comprising two inner layers of the poly(ethylene oxide) film and two outer layers of the non-woven, textile or paper material, the laminate having seal lines bonding the inner and outer layers to one another arranged so as to define one or more closed, non-connecting pockets between the inner layers of the laminate.
6. A product according to Claim 5 wherein each inner layer is laminated continuously to its corresponding outer layer.
7. A product according to Claim 5 or 6 wherein the sachet is formed from a laminated substrate comprising a single ply of the poly(ethylene oxide) film and a single ply of the non-woven, textile or paper material, the laminated substrate being folded during manufacture of the product so as to provide the two inner layers of poly(ethylene oxide) film and the two outer layers of the non-woven, textile or paper material.

Patentansprüche

1. Ein Waschmittelprodukt, das eine teilchenförmige Waschmittelzusammensetzung enthält, die freisetzbar in einem Ein- oder Mehrkammersäckchen enthalten ist, das aus einem thermoplastischen Film aus wasserlöslichem Polyethylenoxid mit einem Molekulargewicht (Viskositätsmittel) von mindestens 1 000 000 gebildet wird oder einen solchen enthält, wobei dieser Film einen äußeren Überzug aus einem flexiblen, durchlöcherten, wasserunlöslichen, jedoch wasserdurchlässigen, blattartigen Vlies-, Textil- oder Papiermaterial aufweist.
2. Ein Produkt nach Anspruch 1, worin das Polyethylenoxid ein Molekulargewicht (Viskositätsmittel) von mindestens 3 000 000 aufweist.
3. Ein Produkt nach Anspruch 1 oder 2, worin das durchlöchernte blattartige Material eine Lochdichte von 3 bis 30 Löchern je cm² aufweist und worin die Löcher durchschnittlich einen Bereich von 0,7 mm² bis 25 mm² einnehmen.
4. Ein Produkt nach einem der Ansprüche 1 bis 3, worin die oder jede Kammer einen geschlossenen inneren Beutel enthält, der aus dem Polyethylenoxidfilm gebildet wird und eine Menge der teilchenförmigen Waschmittelzusammensetzung enthält, wobei der geschlossene innere Beutel enthalten ist in einem und bedeckt wird durch einen äußeren Beutel, der aus dem wasserunlöslichen, jedoch wasserdurchlässigen blattartigen Material gebildet wird.
5. Ein Produkt nach einem der Ansprüche 1 bis 3, worin das Säckchen in Form eines Laminats vorliegt, das zwei innere Schichten des Polyethylenoxidfilms enthält und zwei äußere Schichten des Vlies-

EP 0 253 566 B1

Textil- oder Papiermaterials, wobei das Laminat Versiegelungslinien enthält, die die inneren und äußeren Schichten miteinander verbinden und so angeordnet sind, daß ein oder mehrere geschlossene, nicht miteinander in Verbindung stehende Taschen zwischen den inneren Schichten des Laminats gebildet werden.

5

6. Ein Produkt nach Anspruch 5, worin jede innere Schicht fortlaufend mit seiner entsprechenden äußeren Schicht laminiert ist.

10

7. Ein Produkt nach Anspruch 5 oder 6, worin das Säckchen gebildet wird aus einem laminierten Substrat, umfassend eine einzige Falte aus dem Polyethylenoxidfilm und eine einzige Falte des Vlies-, Textil- oder Papiermaterials, wobei das laminierte Substrat während der Herstellung des Produktes so gefaltet ist, daß die beiden inneren Schichten aus dem Polyethylenoxidfilm und die beiden Außenschichten aus dem Vlies-, Textil- oder Papiermaterial geschaffen werden.

15 Revendications

20

1. Produit pour la lessive, qui comprend une composition de lessive particulaire contenue de façon libérable dans un sachet à un seul compartiment ou à plusieurs compartiments formé d'un - ou comprenant un - film thermoplastique de poly(oxyde d'éthylène) soluble dans l'eau ayant une masse moléculaire moyenne en viscosité d'au moins 1 000 000, ledit film comportant une enveloppe externe de matière en feuille de textile ou de papier, non tissée, flexible, ajourée, insoluble dans l'eau mais perméable à l'eau.

25

2. Produit selon la revendication 1, dans lequel le poly(oxyde d'éthylène) a une masse moléculaire moyenne en viscosité d'au moins 3 000 000.

30

3. Produit selon la revendication 1 ou 2, dans lequel la matière en feuille ajourée a une densité de jours de 3 à 30 jours par cm² et dans lequel les jours ont, en moyenne, une surface de 0,7 mm² à 25 mm².

35

4. Produit selon l'une quelconque des revendications 1 à 3, dans lequel le compartiment ou chacun des compartiments comprend une poche interne fermée formée du film de poly(oxyde d'éthylène) et contenant une quantité de la composition détergente particulaire, la poche interne fermée étant contenue au sein d'une poche externe, qui la recouvre, formée de la matière en feuille insoluble dans l'eau mais perméable à l'eau.

40

5. Produit selon l'une quelconque des revendications 1 à 3, dans lequel le sachet se présente sous la forme d'un stratifié comprenant deux couches internes du film de poly(oxyde d'éthylène) et deux couches externes de la matière de textile ou de papier non tissée, le stratifié comportant des lignes de collage, joignant les couches internes et externes les unes aux autres, disposées de manière à définir une ou plusieurs poches fermées, non communicantes, entre les couches internes du stratifié.

45

6. Produit selon la revendication 5, dans lequel chaque couche interne est stratifiée en continu sur sa couche externe correspondante.

50

7. Produit selon la revendication 5 ou 6, dans lequel le sachet est formé d'un substrat stratifié comprenant une seule épaisseur du film de poly(oxyde d'éthylène) et une seule épaisseur de la matière de textile ou de papier non tissée, le substrat stratifié étant replié au cours de la fabrication du produit de manière à constituer les deux couches internes de film de poly(oxyde d'éthylène) et les deux couches externes de matière de textile ou de papier non tissée.

55